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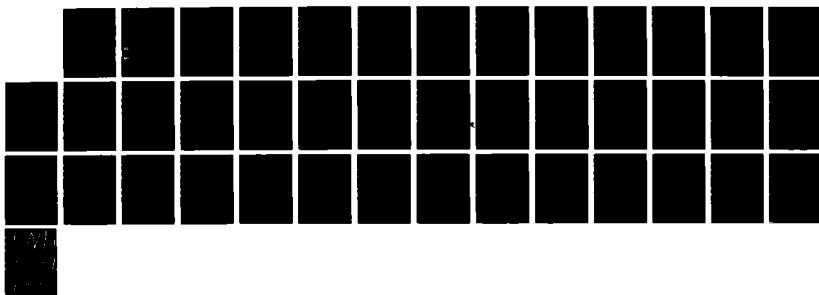
GROUP CONTRIBUTION ANALYSIS OF THE DAMPING BEHAVIOR OF  
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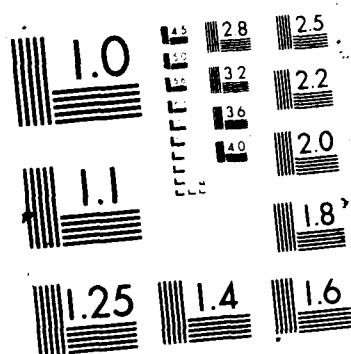
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GROUP CONTRIBUTION ANALYSIS OF THE DAMPING  
BEHAVIOR OF HOMOPOLYMERS, STATISTICAL COPOLYMERS,  
AND INTERPENETRATING POLYMER NETWORKS  
BASED ON ACRYLIC, VINYL, AND STYRENIC MERS

M. C. O. Chang, D. A. Thomas\*, and L. H. Sperling

Polymer Science and Engineering Program  
Department of Chemical Engineering  
Materials Research Center #32  
Lehigh University, Bethlehem, Pennsylvania 18015

\*Department of Materials Science and Engineering

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# ABSTRACT

The integral of the loss modulus versus temperature plots in the vicinity of the glass transition temperature (loss area, LA) was characterized for various homopolymers, statistical copolymers and interpenetrating polymer networks, (IPN's) based on acrylics, vinyls, and styrenic mers. The quantity LA was found to be a molecular characteristic, governed by the structure of the individual mers. The LA of both IPN's and statistical copolymers obeys an additive relation of the component polymers. A group contribution analysis for LA was developed, in which each moiety contributes a specific value to LA. A table derived via this group contribution analysis permits the prediction of LA values. The results show that backbone motions and the moieties attached directly to the backbone contribute the most to the damping peak, and that long side chains act as diluents.

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## INTRODUCTION

When polymers undergo vibration near their glass transition temperature,  $T_g$ , some of the mechanical energy is absorbed as heat, i.e., as increased thermal motion. The fraction of energy absorbed reaches a maximum near the frequency and temperature defining  $T_g$ . The loss modulus,  $E''$ , measures the conversion of mechanical energy to molecular motion (1).

The glass transition results from large-scale conformational motion of the polymer chain backbone, such rearrangements involving a mechanism of hindered rotation around the main chain. Hence, all moieties making up the polymer mer contribute to the glass transition. The main chain motions also satisfy the de Gennes (2) reptation model, where the chains move back and forth in snake-like motions.

Several papers have examined some facets of the areas of interest to the present work (3-14). Among these papers, Kawaguchi (3) found that the area under the  $\tan \delta$ -temperature peak of the  $\gamma$ -relaxation was linearly proportional to the number of methylene units in a series of nylons. Wada, et al. (4) correlated the notched Izod impact strength of various polymers to

the area under the  $\tan\delta$  vs. temperature curves. Read, et al. (5) used areas under the loss modulus vs. reciprocal temperature (at constant frequency) to obtain the average activation energy for the relaxation processes. Heijboer (6) proposed the use of areas under a shear loss modulus vs.  $1/T$  plot to measure the "strength of relaxation". Oberst (7) suggested that the area under the loss modulus vs. temperature plots divided by the glassy storage modulus is approximately constant for amorphous polymers.

Interpenetrating polymer networks, IPN's, are a combination of two polymers in network form (15). Usually, at least one is synthesized and/or crosslinked in the immediate presence of the other. Because the introduction of crosslinks in IPN's restricts the domain size and enhances the degree of mixing, some IPN's exhibit a microheterogeneous domain morphology. Such materials have broad glass transitions, which are potentially useful in sound and vibration damping because they damp well over broad temperature ranges (15-29).

Sperling and Thomas (16-19) investigated broad-temperature damping materials using latex IPN's made from acrylic polymers. Klempner and coworkers (28) studied the cross-polyurethane-inter-cross-epoxy

IPN foams. In an impedance tube absorption method, they found that those IPN foams showed superior sound absorption at all frequencies compared to pure polyurethane foams. Hourston and McCluskey (22) made a cross-poly(vinyl isobutyl ether)-inter-cross-poly(methyl acrylate) sequential IPN, noting one broad loss modulus peak ranging from -20 to +20 °C.

Foster, et al. (20) prepared a cross-poly(n-butyl acrylate)-inter-cross-poly(n-butyl methacrylate) 50/50 sequential IPN filled by 6 vol-% graphite. They found that graphite increased the absolute value of  $\tan \delta$  and the integral of  $E''$ -temperature curve. The IPN subject has been recently reviewed (15, 30-31).

To obtain a better understanding of the glass transition, Fradkin, et al. (32) characterized the integral of the  $E''$  vs. temperature (areas under the linear loss modulus vs. temperature curves). During an investigation of acrylic/methacrylic IPN's, they found that the areas were invariant for a given composition, independent of decrosslinking or subsequent annealing. This result strongly suggested that the areas were determined by the structures of the individual chains, i.e., they are molecular characteristics. By using various acrylic and methacrylic polymers, Chang, et al. (33) found that the integral of the  $E''$ -temperature plots (loss area, LA) for various IPN's obey an

additive relation. Chang, et al. (33) used the additivity concept to develop a group contribution analysis for LA, where each moiety contributes specific values to the area.

In this paper, the integral of the loss modulus vs. temperature curve is characterized to develop a relationship between the extent of damping and the contribution from each group from a broad range of acrylic, vinyl, and styrenic polymers. For completion, values from Reference 33 are included in this paper.

#### THEORY

Physical quantities for which group contribution methods have been applied are molar volume, cohesive energy, solubility parameter, glass transition temperature, heat of fusion, entropy of fusion, molar heat capacity, molar parachor, and others (34). Fedors (35) proposed a system of group contribution to the molar volume of polymers at 298 K ( $V_{(298)}$ ). Bunn (36) applied the group contribution analysis to the cohesive energy of polymers ( $E_{coh}$ ). According to Hildebrand's thermodynamics, Small (37) and Hoy (38) demonstrated that the combination  $(E_{coh} V_{(298)})^{1/2} = F$ , the molar attraction constant, is a useful additive



quantity. Via the molar attraction constant of each moiety in the mer, the solubility parameter of polymers can be predicted, widely used for the estimation of polymer-solvent interaction. Several authors (34, 39-41) have also proposed group contribution analysis for glass transition properties. According to the Fox equation relating the glass transition and composition of copolymers, the moieties in the mer provide weighted additive contributions to  $T_g$ . This concept was widely used by the several authors above in their own group contribution analysis.

By examining the area under the glass transition, a quantitative analysis of group contributions can also be made. The group contribution analysis for LA is based on the assumption that the structural groups in the repeating units provide a weight fraction additive contribution to the total loss area. The basic equation for the group contribution analysis of LA is (33),

$$LA = \sum_{i=1}^n \frac{(LA)_i M_i}{M} = \sum_{i=1}^n \frac{G_i}{M} \quad (1)$$

where  $M_i$  is the molecular weight of the  $i$ th group in

the repeating unit,  $M$  is the molecular weight of the whole mer,  $G_i$  is the molar loss constant for the  $i$ th group,  $(LA)_i$  is the loss area contributed by the  $i$ th group, and  $n$  represents the number of moieties in the mer. Equation (1) provides a predictive method for LA values via the structure of the polymer.

The area under an infrared curve provides a quantitative measure of the concentrations of the moiety causing the particular absorption. Infrared spectroscopy and dynamic mechanical spectroscopy have a good deal in common; both measure aspects of molecular relaxation (42). Dynamic mechanical spectroscopy involves interactions of a periodic mechanical force field with the structural units of the material, resulting in formation of specific peaks in which the interactions show resonance. On the other hand, the infrared absorption peaks result from moieties interacting with electromagnetic radiation.

The vibration frequencies of these two spectra are different, note that dynamic mechanical spectroscopy is in the sonic region. Polymers investigated by both methods show a longitudinal displacement of long chain motion, following the de Gennes reptation model (2). In infrared spectroscopy, all the contributions from moieties can be resolved. However, in the dynamic mechanical spectroscopy of the

glass transition region, all the moieties of the polymer molecule are combined into a nonresolved resonance peak. Both phenomena, in their own ways are subject to the laws of quantum mechanics. Infrared spectroscopy carried out at one frequency as a function of temperature, and dynamic mechanical spectroscopy as a function of frequency at one temperature are less often reported because of the lack of range and instrumental difficulties.

When one attempts to resolve the  $(LA)_i$  contributions, a series of simultaneous equations results, with one more unknown than equations. The extra unknown is the backbone structure common to all the materials in this investigation,  $-CH_2-\underset{|}{CH}-$ . The family of equations have the general form,

$$LA_p = w_b * (LA)_b + \sum w_i * (LA)_i \quad (2)$$

where  $LA_p$  is the LA value for the polymer in question, the subscript b represents the backbone, and the subscript i all other moieties in the polymer.

The quantity  $(LA)_b$  can be determined in two ways: (1) By trial and error, until consistent values are obtained throughout the family of polymers, or (2) By study of polymers with long aliphatic side groups. Then substantially the whole polymer consists of  $-CH_2-$

groups. Both methods are employed below. After the backbone value is determined, the remaining moieties can be systematically evaluated.

## EXPERIMENTAL

### Synthesis

All monomers were dried and freed from inhibitor by a column chromatographic technique using neutral alumina (43). A series of crosslinked homopolymers, statistical copolymers, sequential IPN's, and polymer blends were synthesized in bulk by a U.V. photopolymerization technique (43). Except for polystyrene being crosslinked by divinyl benzene, tetraethylene glycol dimethacrylate (TEGDM) was used as the crosslinking agent. Tables I to III show the polymers studied. For the homopolymer or statistical copolymer synthesis, mixtures of monomer(s), crosslinker, and benzoin was poured into a glass mold fitted with an EPDM rubber cord gasket and exposed to U.V. light for 72 hours.

The IPN's (33) were prepared by swelling polymer

network I in a mixture of monomer II, crosslinker, and benzoin, and polymerized in situ to make sequential IPN's. By a similiar method, poly(vinyl methyl ether)/polystyrene blend was prepared by dissolving poly(vinyl methyl ether) in styrene and benzoin mixture, then polymerized. The resulting samples were dried in a vacuum oven until constant weight was reached to assure the removal of unreacted monomer. The compositions of statistical copolymers and polymer blends were investigated by Mattson Sirius 100 Fourier transform infrared spectrometer using 0.6 wt-% THF-solutions.

Commercial polymers used herein include poly(vinyl chloride), poly(vinyl acetate), a vinyl acetate-vinyl alcohol copolymer, and a styrene-acrylonitrile copolymer (Polysciences Company). These polymers were dissolved in suitable solvents, precipitated by nonsolvents, dried in a vacuum oven, then molded in a hot-press for Rheovibron measurements.

#### Dynamic Mechanical Spectroscopy

An Autovibron Dynamic Viscoelastomer (Rheovibron DDV-III-C type, Toyo Baldwin Co. Ltd.) coupled with a computer and a plotter (assembled by Imass, Inc.) was

used to obtain the storage modulus,  $E'$ , loss modulus,  $E''$ , and the loss tangent,  $\tan\delta$  ( $=E''/E'$ ). The heating rate was approximately  $1^\circ\text{C}/\text{min}$ , and the frequency was set at 110 Hz.

In order to calculate LA, all of the classical semi-logarithmic plots of loss modulus vs. temperature were replotted with the corresponding linear axes. An aluminum plate was used to obtain the background  $\tan\delta$ . Its  $\tan\delta$  is around  $10^{-4}$  at room temperature. The background loss of this Rheovibron system was about  $\tan\delta = 0.03$ , which was subtracted as shown in Figure 1. The background loss modulus, calculated from  $0.03 * E'$  of the polymer, decreases near  $T_g$ , as shown.

Because the value of complex modulus (or storage modulus) can affect the loss modulus value, the Rheovibron was also calibrated by the aluminum plate. After calibration, the storage modulus of a polystyrene sample at  $25^\circ\text{C}$  (110 Hz) was found to be  $2.85 * 10^{10}$  dyne/cm<sup>2</sup> in comparison with the values of 2.3 to  $3.3 * 10^{10}$  dyne/cm<sup>2</sup> (44) by ASTM test method D638.

## RESULTS

All samples were cut to appropriate dimension, and their loss moduli determined as a function of temperature on the Rheovibron. Figure 1 shows the linear loss modulus vs. temperature plot for cross-poly(methyl acrylate)-inter-cross-poly(ethyl methacrylate), PMA/PEMA, 55/45 IPN. (In the classical logarithmic loss modulus vs. temperature plot, this IPN shows a relative broad curve instead of a sharp peak shown in Figure 1.)

Due to the highly crystalline nature of polyethylene and arguments concerning its glass transition (45), it was quite difficult to estimate the LA value of the backbone of "amorphous" linear polyethylene, or rather  $-\text{CH}_2-\dot{\text{C}}\text{H}-$ , the basis for vinyl, acrylic, and styrenic polymers. Starting with the LA's of the polyacrylate homologous series (33), a series of simultaneous equations were written containing one more unknown (the LA of backbone) than equations, i.e.,

$$(\text{LA})_{\text{ac}} = w_b * (\text{LA})_b + w_{\text{ester s.g.}} * (\text{LA})_{\text{ester s.g.}} \quad (3)$$

where,  $(LA)_{ac}$ ,  $(LA)_{\text{ester s.g.}}$ , and  $(LA)_b$  are the LA values of polyacrylate polymers, ester side group, and backbone, respectively, and  $w_b$  and  $w_{\text{ester s.g.}}$  are the weight fractions of backbone and ester side group, respectively. The backbone value was estimated by trial and error until a constant increment of LA of the methylene group was obtained and to obtain the best overall fit, see Figure 2. Thus an  $(LA)_b$  of 3.4 GPa K was obtained.

Using another method, it is assumed that with lengthening the side group in polymethacrylate series, the  $\alpha$  and  $\beta$  relaxations will be diminished in magnitude to an asymptotic value of LA for  $-\text{CH}_2-\text{CH}_2-$  group. Figure 3 shows LA's of polymethacrylate series versus no. of carbons of the ester side groups, a similar value of 3.4 GPa K was obtained for the backbone. Figure 2 also showed the extrapolated LA value for ester moiety of acrylate polymers. Once the backbone value was determined, all of the other moieties could be determined by application of equation (2), where the number of unknowns equalled the number of equations.

Table IV summarizes loss areas,  $(LA)_i$  and molar loss constants,  $G_i$ , for a number of moieties derived from group contribution analysis. The values shown in Table IV are reproducible to within  $\pm 8\%$ .



### The Additive Mixing Rule

As a corollary to equation (1), an additive mixing rule can be written,

$$LA = w_I * (LA)_I + w_{II} * (LA)_{II} \quad (4)$$

where  $w_I$  and  $w_{II}$  are the weight fractions of components I and II in IPN's, statistical copolymers, etc. A plot was made of the calculated LA's from equation (4) vs. the experimental values, Figure 4, for the statistical copolymers and IPN's available. Figure 4 shows that LA obeys the simple additive mixing rule, equation (4), within experimental error for both IPN's and statistical copolymers. For example, the linear loss modulus-temperature plot of cross-poly(n-butyl methacrylate)-inter-cross-polystyrene and the corresponding statistical copolymer with nearly 50/50 compositions are shown as Figure 5. Although the shape of the curves for those two polymers are different, their LA's are the same within experimental error. This suggests that the integral of the loss modulus vs. temperature curve in the vicinity of glass transition is a molecular characteristic, governed by the structure of the polymers.

## DISCUSSION

A schematic diagram for LA behavior of polymer mixtures is shown as Figure 6. In this figure, several polymer mixtures are made from the same polymer pair but by different combining methods, forming systems from low to high miscibility. These are : (a) totally immiscible; (b) with limited miscibility; (c) microheterogeneous systems; and (d) statistical copolymers or miscible systems. Although the miscibility of these four systems is different, the total ability of each to convert mechanical energy into coordinated molecular motion is the same, i.e., they have the same LA value. The loss area depends on the nature of each moiety, independent of environments of the moieties.

Equation (1) shows that LA depends only on the polymer's structure. If more than one type of mer exists in the system, the logic can be extended to include all possibilities, whether the mers are in the same chains or different chains.

### A Sample Calculation

From equations (1) and (4), the group contribution analysis can be utilized to determine LA for unknown systems. This analysis has the predictive ability for damping. For example, the LA value for a PS/PMA 33/67 statistical copolymer (S-9), from equations (1) and (4), and Table IV can be calculated:

$$L.A. = 0.33 * \frac{91.8+916}{104.2} + 0.67 * \frac{91.8+936-42.0*1}{86.1} \quad (5)$$

$$L.A. = 10.9 \quad (6)$$

The observed LA for S-9 is 11.2; the error is about 3%.

Moieties situated at different positions on the mer have different LA values. In particular, both chlorine and nitrile were studied in two positions, both on the backbone and off. The smaller value for chlorine attached to the backbone may be a consequence of poly(vinyl chloride)'s large beta peak.

The inversion of position yields approximately the same damping properties, however, see  $-\text{COO}-$  and  $-\text{OCO}-$ . The LA carboxylic acid value derived from poly(acrylic acid) is similar to the LA value of  $-\text{COO}-$  extrapolated from LA's of polyacrylate homologous series, see Figure 2. It seems that the

structural group or moiety is the smallest unit in LA analysis and complex side groups consisting of several moieties have unique LA values. From Table IV, generally, polar side groups not attached to the backbone contribute more damping capability compared with nonpolar side groups. Hydrocarbon side groups, e.g., isobutyl, cyclohexyl, methylene, and benzyl only give small positive or even negative contributions to LA's. Large side chains appear to act as a diluent. The backbone and groups immediately attached to it constitute the main damping capability.

It should be noted that the value of the complex modulus (or storage modulus) can affect the loss modulus value, i.e.,  $E^* \sin \delta = E''$  (or,  $E' \tan \delta = E''$ ). Hence, the modulus of the dynamic mechanical measurement must be calibrated to obtain an accurate LA value. The LA's shown in Table IV were collected in the condition of storage modulus of a polystyrene sample equal to  $2.85 \times 10^{10}$  dyne/cm<sup>2</sup> (25°C, 110 Hz), see "Experimental".

The LA's were calculated for some homopolymers and multicomponent polymers of various workers (7, 19, 20, 21, 25, 29, 46-47) by the present group contribution analysis method. The background loss which original workers did not apply was neglected. Loss curves of homopolymers were made to be

symmetrically centered around the glass transition. LA's of polymethacrylate polymers (including the  $\beta$ -relaxation) were from the preceding work (33). After the calculations, the conclusion can be drawn that most of the data agree with the present work within  $\pm 15\%$  error, if the modulus is calibrated before calculating LA's, see Table V. The correction factor in Table V is the factor used by us to multiply the storage modulus (or loss modulus) of the various workers in order to calculate the LA's by using Table IV.

The values shown in Table IV are useful in understanding the molecular motion of a polymer chain. If one starts with the de Gennes reptation concept (2), it is obvious that the main chain moves in a back and forth motions. However, long side chains and groups attached to them behave independently. While the main chain motions appear in the glass transition region, side groups motions appear elsewhere, as beta peaks, etc. Most importantly, the notion of the loss modulus for polymers is put on a quantitative basis.

While the experimental data in this paper are quantitatively described by the group contribution method, two additional factors need to be borne in mind:

1. The LA's may depend on the mer surroundings to some extent. Polar solvents, hydrogen-bond forming surroundings, etc. may introduce noticeable effects, as they do in infrared spectroscopy.

2. Morphological features may be important in phase separated materials. The introduction of crystalline regions will reduce the amorphous portions of the polymer, reducing LA accordingly.

## CONCLUSIONS

The area under the loss modulus-temperature curve in the vicinity of the glass transition, LA, is molecular characteristic, which is quantitatively determined by the molecular structure of the polymer material. LA's of both IPN's and statistical copolymers obey an additive equation for component mers. A group contribution analysis was developed which provides a method for predicting LA values via the architecture of the polymers. This analysis may help to select polymers with specified damping

characteristics and provides a quantitative basis for developing new theories of molecular motion near the glass transition temperature.

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## Table Captions

Table I. Homopolymers.

Table II. Statistical copolymer compositions.

Table III. IPN and polymer blend compositions.

Table IV. Group contribution to LA.

Table V. Correction factor for LA's.

Table I. Homopolymers

Sample	Polymers	TEGDM
H-1	poly(methyl acrylate)	1 to 25 mole-%
H-2	poly(ethyl acrylate)	4 mole-%
H-3	poly(n-propyl acrylate)	4 mole-%
H-4	poly(n-butyl acrylate)	4 mole-%
H-5	poly(n-hexyl acrylate)	4 mole-%
H-6	poly(methyl methacrylate)	4 mole-%
H-7	poly(ethyl methacrylate)	4 mole-%
H-8	poly(n-propyl methacrylate)	4 mole-%
H-9	poly(n-butyl methacrylate)	4 mole-%
H-10	poly(n-hexyl methacrylate)	4 mole-%
H-11	poly(n-octyl methacrylate)	4 mole-%
H-12	poly(cyclohexyl acrylate)	4 mole-%
H-13	poly(isobutyl acrylate)	1 mole-%
H-14	poly(2-cyanoethyl acrylate)	1 mole-%
H-15	poly(2-chloroethyl acrylate)	1 mole-%
H-16	poly(benzyl acrylate)	1 mole-%
H-17	poly(acrylic acid)	1 mole-%
H-18	polystyrene	4 mole-% DVB
H-19	polypropylene	none
H-20	poly(vinyl chloride)	none
H-21	poly(vinyl acetate)	none

Table II. Statistical Copolymer Compositions




Sample	Polymers	Weight ratio*	TEGDM
S-1	PMA/PMMA	25/75	1 wt-%
S-2	PMA/PMMA	50/50	1 wt-%
S-3	PMA/PMMA	75/25	1 wt-%
S-4	PnBMA/PS	79/21	none
S-5	PnBMA/PS	57/43	none
S-6	PnBMA/PS	28/72	none
S-7	PMA/PS	83/17	none
S-8	PMA/PS	58/42	none
S-9	PMA/PS	33/67	none
S-10	vinyl acetate/ vinyl alcohol	87/13	none
S-11	styrene/ acrylonitrile	82/18	none

\* Samples S-4 to S-11 were characterized by FTIR. In all cases, agreement with monomer feed compositions was  $\pm 10\%$ .

Table III. IPN and Polymer Blend Compositions

Sample	Polymers	weight ratio	TEGDM
<u>Interpenetrating Polymer Networks</u>			
IPN-1	PMA/PMA	54/46	1 mole-%/1 mole-%
IPN-2	PEA/PEA	57/43	1 mole-%/1 mole-%
IPN-3	PEA/PEA	48/52	2 mole-%/2 mole-%
IPN-4	PMA/PMMA	48/52	1 mole-%/4 mole-%
IPN-5	PMA/PMMA	58/42	1 mole-%/1 mole-%
IPN-6	PMA/PEMA	56/44	1 mole-%/4 mole-%
IPN-7	PMA/PEMA	55/45	1 mole-%/1 mole-%
IPN-8	PEA/PMMA	72/28	2 mole-%/4 mole-%
IPN-9	PEA/PMMA	63/37	1 mole-%/1 mole-%
IPN-10	PEA/PEMA	56/44	1 mole-%/1 mole-%
IPN-11	PnBMA/PS	34/66	1 mole-%/1 mole-%
IPN-12	PnBMA/PS	57/43	1 mole-%/1 mole-%
IPN-13	PnBMA/PS	79/21	1 mole-%/1 mole-%
<u>Polymer Blends</u>			
B-1	PVME/PS	46/54	none

Table IV. Group Contribution to LA

Group	Group location	(LA) <sub>i</sub> (Gpa K)	G <sub>i</sub> (Gpa K) (g/mole)
$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	1	3.4	91.8
$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{O}-( )-\text{H} \end{array}$	2	20.8	936
$\begin{array}{c} \text{O} \\    \\ -\text{O}-\text{C}-( )-\text{H} \end{array}$	2	20.1	905
$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{OH} \end{array}$	2	20.8	936
	2	11.9	916
$-\text{CH}_3$	2	11.0	165
$-\text{OCH}_3$	2	21.7	674
$-\text{C}\equiv\text{N}$	2	23.2	603
$-\text{O}-\text{H}$	2	4.7	80
$-\text{Cl}$	2	9.2	327
	3	3.5	287
	3	2.2	166
$-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_3$	3	-1.7	-98
$-\overset{ }{\text{CH}}-$	3, 4	0.5	7
$-\text{CH}_2-$	3	-3.0	-42
$-\text{C}\equiv\text{N}$	3	14.5	377
$-\text{Cl}$	3	15.7	556

1. Backbone.

2. Side group attached to backbone directly.

3. Side group not attached to backbone.

4. Value derived from isobutyl side group.



Table V. Correction Factor for LA's

Group	Ref.	Polymers <sup>a</sup>	Storage modulus, Gpa <sup>a,b</sup>	Corr. factor <sup>c,d</sup>
Foster, et al.	20	PnBA, PnBMA, and IPN's based on ac- rylic polymers	3.05 (PnBMA, glassy state)	1.0
Widmaier, et al.	21	PS, PnBA, and IPN's based on PS/PnBA	2.75 (PS, room temperature)	ca. 1.0
Hourston, et al.	25	IPN's based on acrylic polymers	for example, 3.0, ( <u>cross-</u> <u>PiBA-inter-</u> <u>cross-PEMA</u> 50/50 IPN, gl- assy state)	ca. 1.0
Oberst	7	Poly(vinyl acetate)	2.5 (PVA, glassy state)	ca. 1.0
Hermant, et al.	29	PMMA	3.3 (PMMA, room temperature)	1.1
Lorenz, et al.	19	IPN's based on acrylic polymers	for example, 1.6 ( <u>cross-poly(EMA-</u> <u>stat-EA)-inter-</u> <u>cross-poly(nBA-</u> <u>stat-EA) (21-</u> <u>stat-9)/(49-stat-</u> 21) IPN glassy state)	1.8
Gillham, et al.	46	PMMA	4.2 (PMMA, room temperature)	0.9
Weiss, et al.	47	PS	1.0 (PS, room temperature)	2.85

a. PnBA : poly(n-butyl acrylate); PnBMA : poly(n-butyl methacrylate); iBA : isobutyl acrylate; EA : ethyl acrylate.

b. Storage modulus measured by different groups. According to Tobolsky (48), Young's modulus of amorphous polymer is proportional to  $\delta^2$  ( $\delta$ ,

Table V. Correction Factor for LA's (continued)

solubility parameter), because most amorphous polymers have the  $\delta$  values from 16 to 20 (J/cm<sup>3</sup>)<sup>1/2</sup>, their glassy modulus are nearly the same, i.e., 3.0 GPa. The storage modulus at the glassy state for amorphous astate can also be roughly estimated by Tobolsky's relation, i.e.,  $E'_{PVA}/E'_{PS}=0.95$ ,  $E'_{PVC}/E'_{PS}=1.17$ ,  $E'_{PMMA}/E'_{PS}=1.34$ , etc.

c. A factor can be multiplied by the loss modulus to calculate LA's.

d. Although each worker may use different frequencies for running dynamic mechanical spectroscopy, it has been explained by the equation (1) of Ref. 33 that frequency carries unimportant effect on LA value.

## FIGURE CAPTIONS

- Fig. 1 Linear loss modulus versus temperature plot for a PMA/PEMA 55/45 IPN. The background correction for  $E''$  is also shown.
- Fig. 2 LA's of the ester group of the polyacrylate homologous series versus the weight fraction of methylene moiety in the ester side group. Also shown is the extrapolated LA value of the ester group.
- Fig. 3 LA's of the polymethacrylate homologous series versus number of methylene groups in the ester side group. The asymptotic value is assumed to be the LA of backbone.
- Fig. 4 Test of additivity of the homopolymer LA's in predicting the corresponding IPN and statistical copolymer LA's.
- Fig. 5 Comparison of an IPN and a statistical copolymer based on poly(n-butyl methacrylate)/polystyrene with nearly 50/50 compositions.
- Fig. 6 Schematic diagram for loss modulus vs. temperature behavior of polymer I/polymer II with different miscibility, (a) totally

immiscible polymer pairs, (b) polymer blends with limited miscibility, (c) microheterogeneous system, (d) miscible system. The weight fraction of each component is 50% for all these systems.

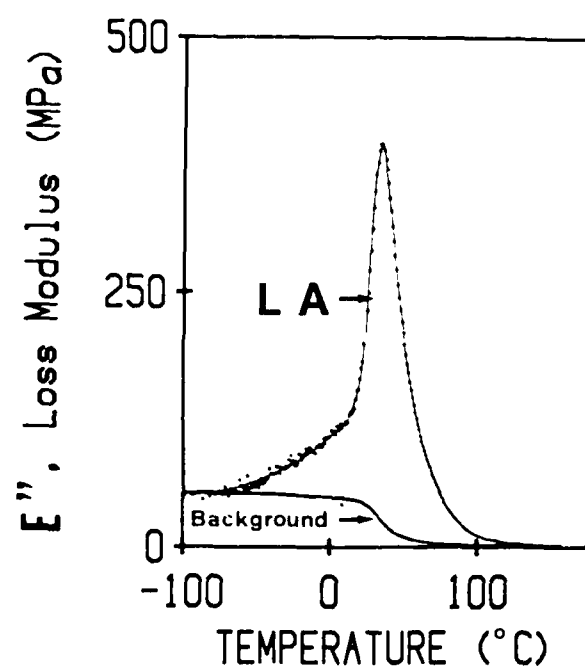


Fig. 1

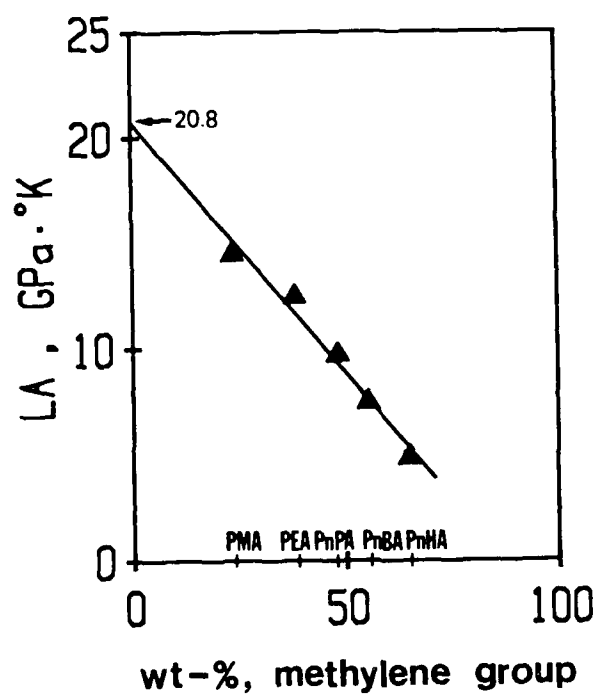


Fig. 2

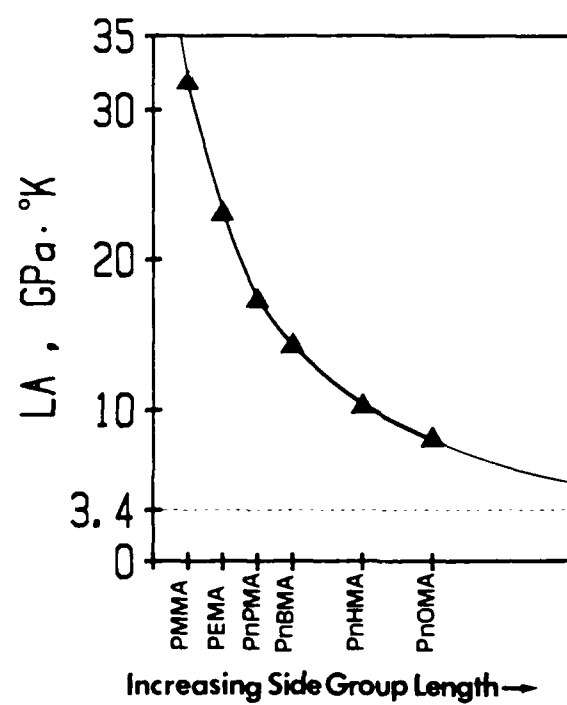


Fig. 3

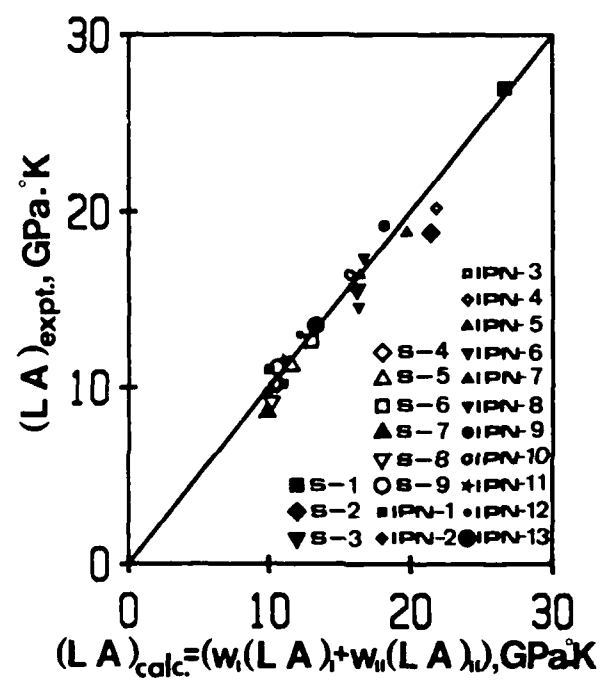


Fig. 4



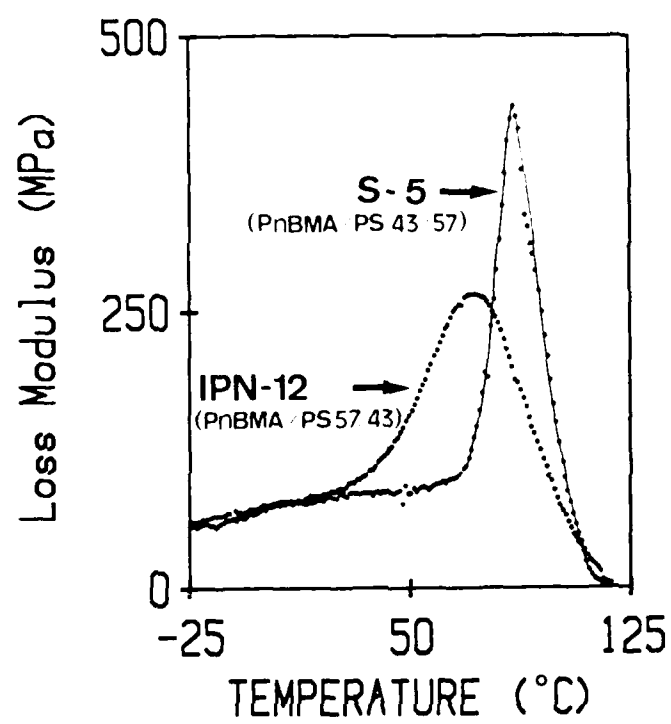


Fig. 5

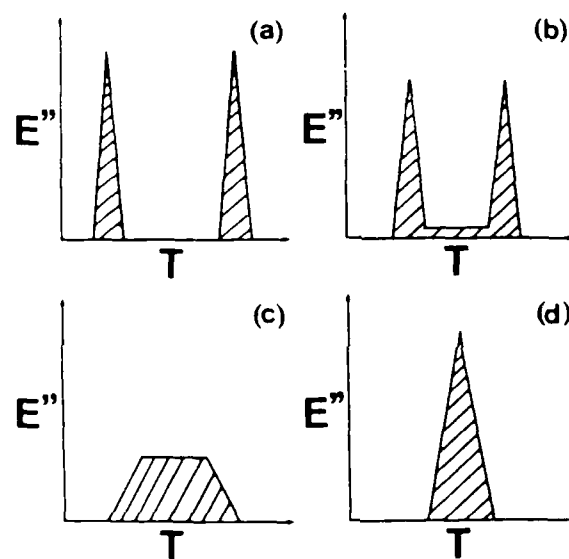


Fig. 6

END

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